INTEGRATED EXAMINATION OF TECHNICAL CONDITION OF MOLYBDENUM BOATS
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Pelletized fuel is used in nuclear power engineering. After press-powder being prepared and pressed the obtained green pellets are converted to high-strength ceramic fuel by sintering in the reducing medium. Sintering is performed continuously in tunnel-type furnaces at 1750 °C. Before being sintered green pellets are subjected to slow heating up to 600-800 °C, and after being sintered – to slow cooling. Total process duration for ceramic pelletized fuel production makes 30-40 hours. During all this period pellets are located in a special container i.e. molybdenum boats.

The important parameter of molybdenum boats is their working capacity that shall comprise 250-300 working cycles taking into account the reconditioning. In practice boats withstand considerably less working cycles. It is explained by the fact that their working capacity is influenced by the chemical composition of structure, construction and characteristics of production practice.

The chemical composition of two suppliers is given as an example in Table 1.

Table 1.

<table>
<thead>
<tr>
<th>Supplier</th>
<th>Chemical composition, %</th>
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<tbody>
<tr>
<td></td>
<td>Mo</td>
</tr>
<tr>
<td>Alloy 1</td>
<td>Basic</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Alloy 2</td>
<td>Basic</td>
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</tbody>
</table>

Alloys are similar according to the chemical composition, but Alloy 1 has no carbon content (C), and Alloy 2 has no oxygen (O₂). Carbon and oxygen are the most harmful impurities for molybdenum because they have a considerable influence on molybdenum liability to brittle failure. The formation of volatile and fusible oxides (Mo - MoO₃) at grain boundaries results in sharp decrease of strength and plasticity.

Molybdenum carbides (Mo C, Mo₂C), locating at grain boundaries, form brittle interlayers where cracks are initiated.

In case of prolonged heating the strength of molybdenum is decreased through the process of secondary re-crystallization, grain coarsening up to wall thickness dimensions of boats, concentrations of stresses at boundaries of coarse grains.

Pressure and internal stresses are increased through hydrogen dissolution, its accumulation in gaseous state in pores, lattice locations and at grain boundaries. It is assumed that the drop of working temperature from 1750 to 1200 °C decreases hydrogen action and increases the number of working cycles in 1.5 – 2 times.
In Figure 1 the example of molybdenum metallographic section structure in the beginning of operation and after 50 working cycles is given.

![Figure 1](image1.png)

_Figure 1 Structure of molybdenum metallographic section before (a) and after (b) 50 sintering cycles._

Fracture examination of molybdenum boat after 70 working cycles witnesses the brittle fracture. The appearance of fragments is given in Figure 2. In the upper part the fracture has dark color (a), and in the lower part – metallic luster (b) inherent to fresh fracture. Thus it can be supposed the fracture is occurred as a result of crack extension.

![Figure 2](image2.png)

_Figure 2. Fragments of molybdenum boat after 70 working cycles._

Metallographic examination of fragment structure shows no substantial change of grain form and dimensions. However segments with abnormally coarse grain are detected in the zone of crack. Grain dimension in these segments exceeds several times the average grain dimension. In Figure 3 the microstructure of these segments is given.
The presence of segments with similar abnormally coarse grains in the material inevitably results in the appearance of secondary stresses (especially during heating and cooling). Besides it should be mentioned the growth of grain dimension results in the considerable shrinkage of boundary length and thus in the growth of brittle phase volume fraction at boundaries. For these reasons the strength of such segments is much lower the strength of metal in total due to the most likely formation of cracks.

Furthermore brittle phase precipitates Mo – Mo$_2$C and Mo – MoO$_3$ were detected at grain boundaries. (Figure 4).

Micro-hardness measurements of this phase show its hardness makes 675 – 756 kgf/mm$^2$, and it is much higher in comparison with molybdenum - 240 – 260 kgf/mm$^2$. The presence of zone with heterogeneous structure and increased stress resulted in plasticity loss and crack formation.
Statistical data on failure of molybdenum boats was collected during a long period of time. In Figure 5 the classical curve of number of working elements depending on time is given.

On the given graphs «I» segment is determined by failure of some working elements due to some initial reject level and other reasons connected with the beginning of operation and run-in of working elements. On «II» segment the number of failures is approximately stationary, therefore on this segment the number of working elements is linearly decreased in the course of time. On «III» segment the number of failures begins to increase due to the fact that elements start to failure because of physical wear. On «I» segment the number of working elements in the instant of time \( t \) can be calculated according to the following formula:

\[
M(t) = M_0 \times F(t)
\]

where \( M_0 \) - initial number of working elements, \( M \) - current number of working elements, and \( F(t) \) - failure rate function for working elements. If it is assumed that on «I» segment the failure of working elements occurs by accident, in this case the dependence \( F(t) \) is represented as follows:

\[
F(t) = \exp(-\lambda t)
\]

where \( \lambda \) - failure rate function. Also the value \( \lambda(t) \) characterizes failure density function provided that the system has been working failure–free during time \( t \). The value \( \lambda(t)dt \) characterizes the probability of the fact that the system will fail within time interval \( t, t+dt \) provided that it did not fail until the instant of time \( t \).

In this connection it should be mentioned that the obtained statistical data related to molybdenum boats was approximated within the limits of the given model. First of all on «I» segment we assumed that failures of molybdenum boats occur by accident, therefore the approximation was exponential that allowed us to estimate the value \( \lambda = 0.017 \). On «II» segment we assumed failure rate of molybdenum boats to be constant resulting in the linear decrease of number of working boats in the course of time, therefore the approximation was linear on «II» segment. It allowed us to determine, firstly, the linear equation of regression, secondly, the amount of cycle to which the number of working boats will decrease to zero. This way we determined the maximum operation period of molybdenum boats. It will happen on 520 cycle. It can be also mentioned that it is unlikely molybdenum boats to be working for so long period of time.
On «III» segment the failure rate highly increases due to the physical wear of molybdenum boats. The physical wear of molybdenum boats first of all is determined by the secondary recrystallization of molybdenum that will result in the mechanical fracture of boat construction. Therefore the obtained estimate allows us to determine the approximate number of cycles when boats can operate in normal condition. This number of cycles can be approximately estimated as 300-350 that is given as the operating life in the report of English researchers [7].

Segments «II» and «III» are the most interesting for the use of non-destructive testing methods in view of remaining life estimation. Methods of non-destructive testing such as visual – measuring method, ultrasonic testing and eddy current method were used.

Wall thickness of molybdenum boats was measured using ultrasonic thickness gauge ЭМАТ-100 and 36DL, and attenuation of ultrasonic waves in molybdenum at frequencies 5MHz and 10 MHz was measured using ultrasonic flaw detector Epoch-III-B.

Cracks were detected as well as the depth of detected defect was estimated using eddy current flaw detector ВД-89НП.

In Figure 6 results of wall thickness measurements are given.

Figure 6. Dependence of wall thickness $d$ on the number of cycles

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In Figure 7 Detection of defects in elements of molybdenum boats
Figure 7. Frequency of defective boats

Literature:
2. I.L.Mirkin, Problems of theoretical material science, M, Oborongiz, 1938, p.3.